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Nitric Oxide Depth-Profiles
of Aged Double-Base Gun Propellants

by R. A. Pesce-Rodriguez and P. E. Marsh

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R. A. Pesce-Rodriguez
Weapons and Materials Research Directorate, ARL

P. E. Marsh
U.S. Army Aberdeen Test Center

Abstract

As part of a propellant/epoxy compatibility study, double-base perforated stick gun propellant was downloaded from tank rounds subjected to temperature/humidity cycling for one month. The propellant was analyzed by traditional HPLC methods and found to have experienced no significant depletion of stabilizer. Analysis by a new desorption-GC-MS method yielded depth-profiles of nitric oxide (NO) that indicated localized decomposition at propellant surfaces. Surfaces of the propellant that had been in direct contact with a layered material (glass-reinforced RTV rubber/RTV rubber/epoxy/composite sabot) showed NO levels well in excess of baseline measurements, and a level somewhat higher than that of exterior surfaces not in direct contact with the layered material. Nitric oxide "enhancement" was observed as deep as 1-mm in from the exterior surfaces. Analysis of samples aged in the lab revealed that some of the NO generated by decomposing propellant diffuses into the silicone in the RTV rubber, thereby removing it from the autocatalytic degradation cycle and resulting in a decreased level of decomposition (as evidenced by NO levels at the core of the propellant). It was observed that uptake of NO by the silicone components was completely reversible. While the NO level at the core of the propellant was found to be lower for the samples exposed to the suspected incompatible material than for the control, elevated NO levels were found at depths up to 0.75 mm from the surface exposed to the suspected incompatible epoxy, confirming the existence of an incompatibility between the propellant and epoxy in the layered material.

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R.A. Pesce-Rodriguez
US Army Research Laboratory, ATTN: AMSRL-WM-BD, Aberdeen Proving Ground, MD 21005-5066
(rose@arl.army.mil)

P.E. Marsh
US Army Aberdeen Test Center, ATTN: CSTE-DTC-AT-WC-C, Aberdeen Proving Ground, MD 21005-5059
(pmarsh@atc.army.mil)

ABSTRACT

As part of a propellant/epoxy compatibility study, double-base perforated stick gun propellant was downloaded from tank rounds subjected to temperature/humidity cycling for one month. The propellant was analyzed by traditional HPLC methods and found to have experienced no significant depletion of stabilizer. Analysis by a new desorption-GC-MS method yielded depth-profiles of nitric oxide (NO) that indicated localized decomposition at propellant surfaces. Surfaces of the propellant that had been in direct contact with a layered material (glass-reinforced RTV rubber/RTV rubber/epoxy/composite sabot) showed NO levels well in excess of baseline measurements, and a level somewhat higher than that of exterior surfaces not in direct contact with the layered material. Nitric oxide "enhancement" was observed as deep as 1-mm in from the exterior surfaces. Analysis of samples aged in the lab revealed that some of the NO generated by decomposing propellant diffuses into the silicone in the RTV rubber, thereby removing it from the autocatalytic degradation cycle and resulting in a decreased level of decomposition (as evidenced by NO levels at the core of the propellant). It was observed that uptake of NO by the silicone components was completely reversible. While the NO level at the core of the propellant was found to be lower for the samples exposed to the suspected incompatible material than for the control, elevated NO levels were found at depths up to 0.75 mm from the surface exposed to the suspected incompatible epoxy, confirming the existance of an incompatibility between the propellant and epoxy in the layered material.

BACKGROUND

As part of an investigation of possible incompatibility of a nitrate ester propellant with a proprietary component of a tank round (an epoxy coating), an analysis of propellant downloaded from fully loaded rounds subjected to temperature and humidity cycling for one month was performed. Analyses of control samples prepared in the lab were also performed. The method used was based on desorption-gas chromatography-mass spectrometry (D-GC-MS), and had been previously developed at the Army Research Laboratory (ARL) for the analysis of nitrate ester gun propellants exposed to conventional and plasma ignition sources as part of the ARL Plasma-Propellant Interactions Program. A report on such an analysis for M30 and JA2 gun propellants was presented at the JANNAF 37th Combustion, 25th Air-breathing Propulsion, 19th Propulsion Systems Hazards, and 1st Modeling & Simulations Subcommittees Joint Meeting. [1] The method has also been successfully applied to the analysis of JA2 gun propellant subjected to shear forces. [2]

The method relies on desorption of NO present in the propellant. All nitrate ester propellants will have some level of NO "trapped" within them, even if they have just been formulated and have what is considered to be sufficient stabilizer present. Stabilizer is added to a formulation to react with nitrate ester degradation products and thereby prevent them from participating in the autocatalytic degradation of the propellant. However, the stabilizer is usually present at a level of less than 1 wt-%, and cannot be in all places at all times. So, analysis of a "stable" nitrate ester propellant by the D-GC-MS method will give a baseline value for NO content that can be used to compare with an identical propellant exposed to degrading forces such as heat, reactive gases, and incompatible materials. Analysis of a number of samples exposed to various degrading forces has

revealed that detection of enhanced NO levels in degraded propellant does not necessarily correspond with a notable decrease in stabilizer level, or with a notable carbonyl peak in FTIR spectra of the samples. The implication is that the D-GC-MS method can be used to detect very low levels of NO in a degrading propellant, and can therefore be used as a very early indicator of propellant instability or propellant/material incompatibility. The method is somewhat labor intensive and requires special equipment, and would not likely ever become part of routine surveillance testing of nitrate ester propellants. However, the method has been shown to be very useful for probing the effect of degrading forces on propellants early in the degradation process, when the effects of these forces cannot be identified by other, more traditional approaches.

For background information on the nucleophylic reactions responsible for the incompatibility of nitrate esters with amides such as those found in the epoxy from this study and in common propellant stabilizers (e.g. diphenylamine, ethyl centralite, and Akardite I and II), the reader is directed to references [3] and [4].

EXPERIMENTAL

Temperature cycling of propellant: Fully loaded tank rounds were subjected to temperature cycling at 95% relative humidity for 28 days, as per the following program:

Step 1: Propellant held at 21 °C for 1 hr
Step 2: Temperature reduced to -54 °C over the course of 2 hr.
Step 3: Temperature held at -54 °C for 5 hr.
Step 4: Temperature raised to 71 °C over the course of 3 hr.
Step 5: Temperature held at 71 °C for 13 hr.
Step 6: Temperature reduced to -54 °C over the course of 3 hr.
Step 7: Repeat steps 3-6 until a total of 28 days has elapsed.

The propellant was a double-base, 19-perf stick. The samples analyzed were in direct contact (on one side only) with a layered material composed of a glass-reinforced RTV rubber, on top of a RTV rubber, on top of an epoxy resin, on top of a composite sabot section. Figure 1 gives a schematic representation of the layered material.
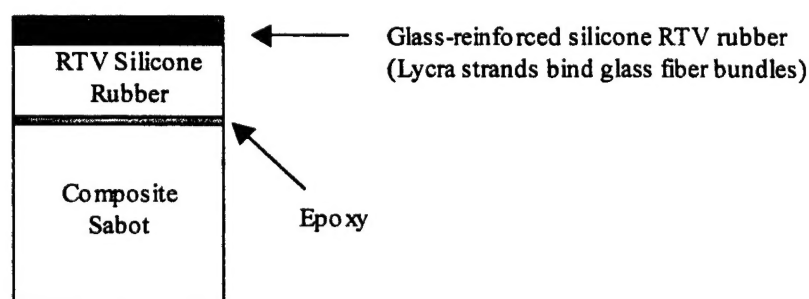

Figure 1. Schematic drawing of layered material

Aging of propellant in the laboratory: Samples of the same nitrate ester propellant used in the fully loaded round, but in 2.5-mm sheets rather than stick geometry, were aged in the lab at 60 °C. Each sample was approximately 2 cm x 1 cm in area. One sample was first placed in contact with the layered material used in the fully loaded round (glass-reinforced RTV rubber/RTV rubber/epoxy/composite sabot). Both the propellant and the layered material were then wrapped

together tightly in a single piece of heavy-duty aluminum foil. The layered material was much larger in area than the propellant sample (approximately 8 cm x 3 cm). The second sample (the control) was wrapped by itself in heavy-duty aluminum foil. Upon opening the oven after 2 months of aging, there was an obvious odor from NOx gases.

Sample preparation for D-GC-MS Analysis: Perforated stick propellant was sliced with a microtome to give cross-sectional slices with a thickness of approximately 50 μm. The slices were trimmed to yield rectangular samples that spanned the diameter of the original sample, but were not more than approximately 3 mm in height. The width and mass of the rectangular sample were measured with a micrometer and microbalance, respectively, and recorded. Slivers (approximately 3-mm in height and 0.3-mm in width) were then cut from the rectangular sample beginning with one end of the rectangle (usually the exposed surface) and working across the rectangle until the whole sample was consumed. The masses of each sliver were measured prior to its analysis. The width of each sliver was estimated by multiplying the total width of the sample by the ratio of the mass of each sliver to the total sample mass.

Sheet propellant was also cut with a microtome to give cross-sectional slices with a thickness of 50 μm. The ends of each slice were trimmed to yield a rectangular sample with width of approximately 3 mm and a nominal height of 2.5 mm, which was dictated by the thickness of the original propellant sheet. (See Figure 2 gives a schematic representation of the sample.) The sample was then treated (weighed, slivered, etc.) as described above for the 19-perf stick sample.
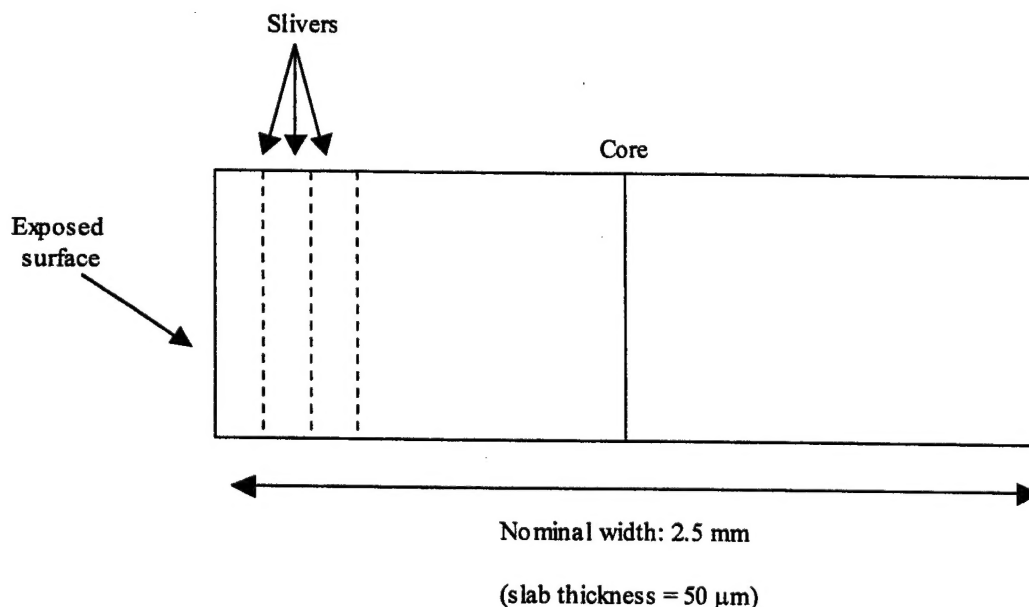
Figure 2. Schematic drawing of slice of double base propellant showing "cut lines" for first 3 slivers.

D-GC-MS: Analysis of NO levels was performed by means of desorption-gas chromatography-mass spectroscopy, D-GC-MS. Desorption was achieved via a CDS Model 2000 Pyroprobe® (coil type) connected through a heated interface chamber to the splitless injector of a Hewlett Packard GC-MS system (Model 5890 GC and Model 5970 MSD). The GC Column used was a J&W Scientific

capillary column (0.32 mm x 25m; 3 m DB-17HT film). The injector temperature was 200 °C; the Pyroprobe® interface temperature was 175 °C. The GC oven temperature program was as follows: 50 °C isothermal for 1 min; 50-250 °C at 40°C/min; 250 °C isothermal for 1 min. The Pyroprobe® was programmed to give a 20-s desorption pulse at 175 °C (heating rate: 1000 °C/sec). Propellant slivers were held within the coil of the Pyroprobe® by first placing them in a quartz tube containing a small plug of glass wool, and then inserting the entire tube into the coil.

Nitric oxide levels in propellant samples were determined via Hewlett Packard ChemStation software by first extracting the selected ion chromatogram (SIC) for m/z = 30, the molecular weight of nitric oxide, from the total ion chromatogram (TIC). An example of a TIC and SIC are given in Figure 3. The peak appearing at approximately 2.5 min in the TIC is due to trapped NO that immediately desorbs from the sliver, as well as to air introduced into the Pyroprobe chamber when the Pyroprobe containing the sample was placed in the interface. The 2.5 min peak in the SIC is due only to the trapped NO. It is integrated and normalized to the mass of the sliver to determine the relative amount of NO trapped in the sliver. Nitric oxide profiles are then constructed by plotting the normalized NO peak areas against the cumulative thickness of the slivers. The large peak appearing near 5.5 min in the SIC is due to nitrate ester plasticizer; the smaller peak near 4 min is due to plasticizer degradation product. Neither of these peaks is used in this analysis.

[Note: NO_2 thermally decomposes to NO in the GC column before reaching the MS detector. Strictly speaking, the profiles obtained using the D-GC-MS method are only for NO, but the NO detected may have originally been either NO or NO_2 in the propellant sample.]
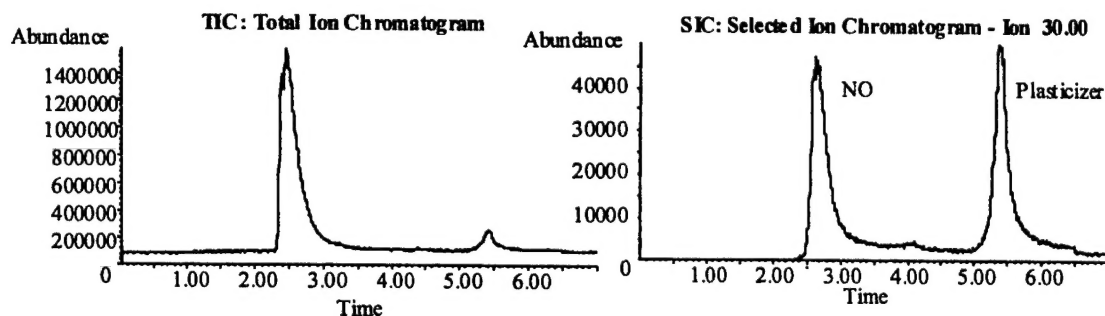

Figure 3. Typical TIC and SIC (m/z = 30) for D-GC-MS analysis of double-base propellant

RESULTS AND DISCUSSION

Analysis of downloaded propellant from fully loaded rounds subjected to temperature cycling at high relative humidity was performed using a standard HPLC method, and found to fall within experimental error of the nominal level of stabilizer (results not shown). Microtransmission-FTIR analysis of the surfaces exposed to the suspected incompatible layered material indicated no notable carbonyl peaks, suggesting that the propellant had not significantly decomposed. (A FTIR spectrum of the exposed surface of the propellant sample compared with a nitrocellulose standard is given in Figure 4.)

However, analysis by the D-GC-MS method described above yielded the NO depth-profile given in Figure 5, and indicated localized decomposition at the propellants surfaces. Surfaces of the propellant that had been in direct contact with the layered material showed NO levels well in excess of baseline measurements, and a level somewhat higher than that of surfaces not in direct contact with the layered material. NO "enhancement" was observed as deep as 1 mm in from the exterior

surfaces. [The solid line near 80 (arbitrary units) on the y-axis is an estimate of baseline NO for the propellant. Actual data is not presented because a propellant sample with the same geometry, and from the same lot, was not available. The average value is from analysis of the same propellant formulation but another geometry.]
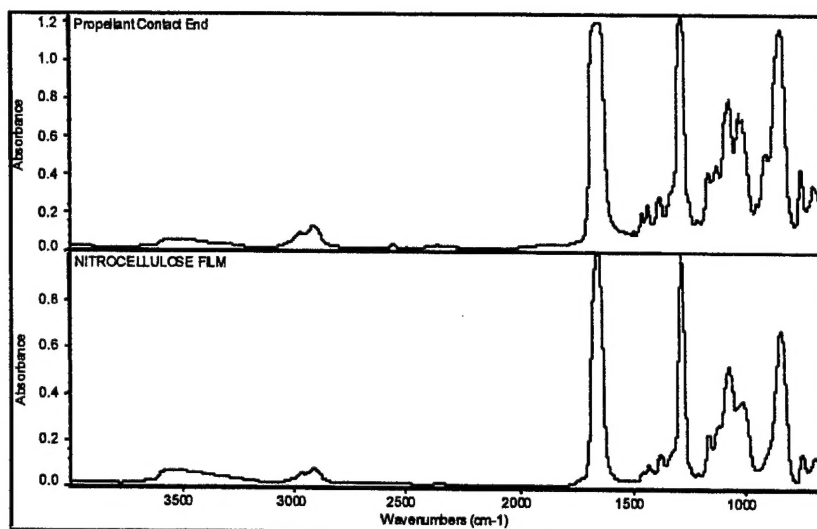

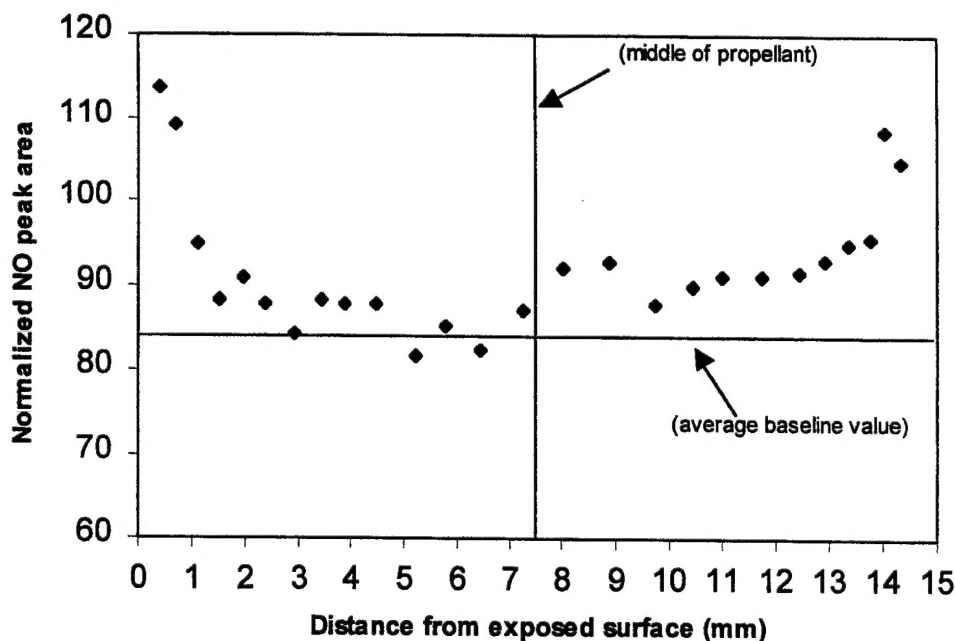**Figure 4.** FTIR spectra of exposed surface of propellant sample compared with nitrocellulose.

Figure 5. NO profile for propellant downloaded from fully loaded round subjected to temperature cycling at 95% RH for 1 month.

Analysis of control samples aged in the lab yielded the NO depth profiles given in Figure 6. The data plotted in gray triangles near 80 (arbitrary units) on the y-axis indicate the baseline measurement of normalized peak area for NO obtained from the analysis of un-aged propellant. That the layered material is incompatible with the propellant is evidenced by the asymmetry in the profile for that sample. Enhancement of the NO level (relative to baseline) is observed at depths up to approximately 0.75 mm from the surface exposed to the suspected incompatible material, but only to approximately 0.05 mm from the side that was not exposed to the material. The profiles for the control sample and the sample in contact with the layered material look very different at the core of the samples. The level at the core of the control sample is nearly identical to that at the surfaces. For the sample exposed to the layered material, the core level is very close to the baseline value. On first inspection, this data was somewhat puzzling. It was expected that the propellant in contact with the layered material would have experienced a greater degree of decomposition because it had been proposed by one of the authors (RP) that the layered material contained components that were incompatible with the propellant. These components were: the epoxy layer and the Lycra strands that hold the glass fibers together in the glass reinforced RTV rubber layer. It was understood that that epoxy layer was not in direct contact with the propellant, but it had been shown in earlier experiments that nitrate ester plasticizers and their decomposition products could easily diffuse across the silicone RTV layers that separated the propellant and the epoxy. In addition, evidence was found that suggested the epoxy catalyzed the decomposition of the nitrate ester plasticizer. [5] It was not immediately obvious why the control sample would have a higher level NO at its core than did the propellant in contact with the suspected incompatible material. Analysis of the layered materials recovered from the laboratory-aged samples provided some insight.
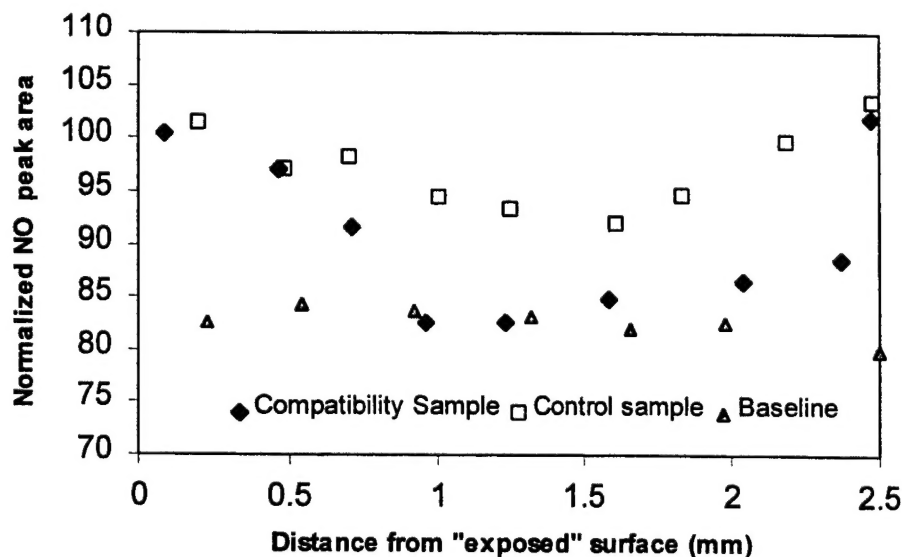

Figure 6. NO profiles for propellant aged in laboratory for 2 months at 60 °C.

D-GC-MS results for the components of the RTV layers that had been in contact with the propellant are given in Figure 7. The glass fibers (no resin) desorbed only a small amount of NO, but no plasticizer; the Lycra fibers from the glass-reinforced RTV layer yielded a relatively large amount of nitrate ester plasticizers and a fair amount of NO (most of the NO is proposed to result from the incompatibility of the Lycra and the nitrate ester plasticizer); the RTV resin from the glass-reinforced

RTV layer yielded both NO and nitrate ester plasticizer, but not nearly as much as did the Lycra fibers. [Note: all samples were approximately the same size.]. The conclusion from the results shown in Figure 7 is that the silicone RTV rubber and the Lycra fibers can at least temporarily absorb some of the NO that might otherwise be available to react with propellant and contribute to its autocatalytic degradation. While it is true that the silicon and Lycra can also absorb nitrate ester plasticizers, removal of these from the environment around the propellant isn't expected to be of consequence because the vapor pressure of the plasticizers in that environment is dictated by the temperature and pressure of that environment. If the Lycra absorbs some of the plasticizer, the partial pressure of the plasticizer will drop and more plasticizer will desorb from the propellant to restore the equilibrium.

By putting together the data in Figures 6 and 7, it may be concluded that the silicone rubber in the layered material may (if only temporarily) stabilize the propellant by absorbing some of the NO generated by decomposing propellant. The absorption capacity of the silicone rubber layers has not been determined, but is expected that it cannot exceed whatever level of NO there happens to be in the propellant environment at any given time. This is because NO is not actually absorbed by the silicone, but rather just diffusing through it. If for some reason the level of NO in the propellant environment were to drop, the NO would diffuse back out from the silicone to re-establish equilibrium. That this occurs was confirmed by analyzing silicone RTV samples from laboratory aging experiments after they had been left under ambient conditions for 4 days. D-GC-MS analysis (results not shown) indicated that the samples had lost all the NO and nitrate ester plasticizers they had absorbed. [Note: the lab-aged samples were wrapped tightly in aluminum foil, so it is likely that much of the NOx generated by the propellant was absorbed by the layered material. The foil wrap was certainly not airtight, as evidenced by the NO odor observed when the over was opened to retrieve samples.]
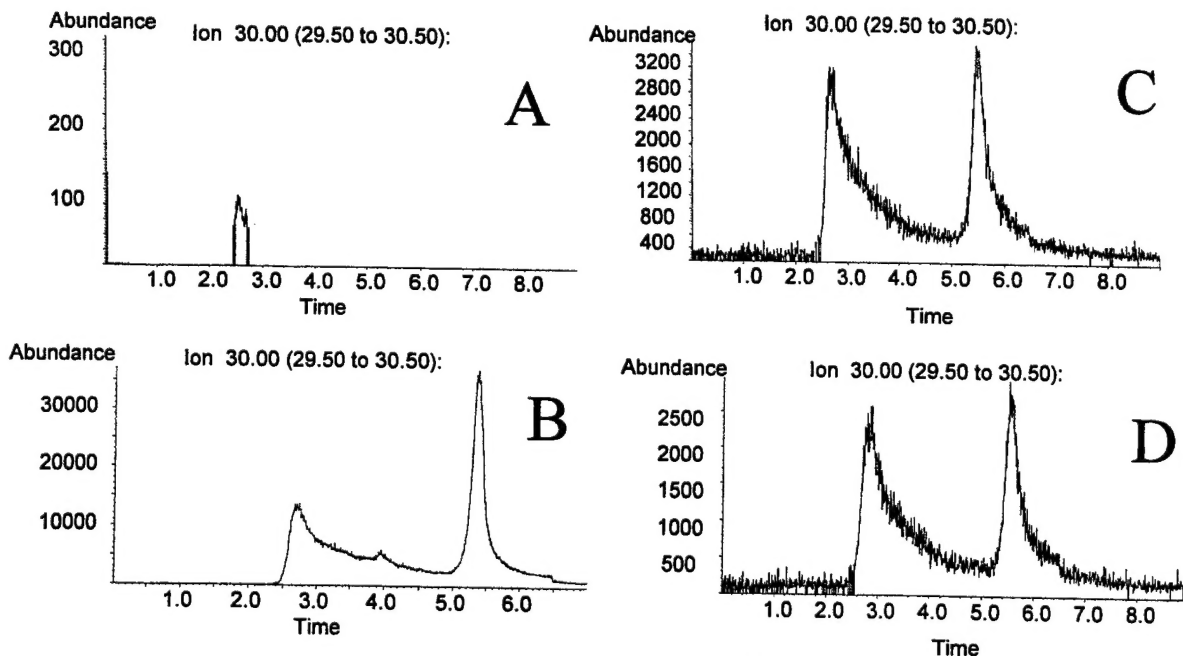

Figure 7. SICs for components of layered material recovered from lab aging sample (in contact with propellant for 2 months at 60 °C). **A:** resin-free glass fibers; **B:** Isolated Lycra fibers (note: scale ~10x that of other chromatograms); **C:** silicone rubber from glass-reinforced layer; **D:** Silicone RTV rubber from layer without glass-reinforcement

It must be noted that for the samples aged in the laboratory, there was a large excess of silicone layered material relative to the amount of propellant (i.e. approximately 0.5 cc of propellant vs. 7.2 cc of layered material), and relatively little free volume around the sample because of the tightly wrapped aluminum foil. In the fully loaded round, the ratio would be much lower, and there would be significantly more free volume. Still, the silicone RTV layered material could serve to stabilize the propellant by absorbing even a fraction of the NOx generated by degrading propellant. However, it is suspected that this stabilizing effect will eventually be overcome by the destabilization induced by the catalytic degradation of the nitrate ester plasticizers absorbed in the Lycra fibers and in the silicone RTV rubber in contact with the epoxy resin.

CONCLUSIONS

A desorption-GC-MS method developed at ARL for the examination of propellant exposed to degrading stimuli has been successfully applied in an aging/compatibility study involving a double-base propellant in contact with a suspected incompatible material. The method produced depth profiles for NO trapped within the propellants studied. Measurements were made for propellant that had been downloaded from fully loaded rounds and for propellant aged in the laboratory. Results were compared with baseline NO levels obtained from untreated samples. In the course of the investigation, it was determined that components of the suspected incompatible layered material (namely silicone-based RTV rubbers) may actually serve to stabilize the propellant (if only temporarily) by absorbing some of the NOx generated by the propellant as it ages. Propellant directly in contact with the layered material was observed to have experienced a greater degree of degradation (as evidenced by its NO profile) than the surface not in contact with the material, suggesting that incompatibility between the propellant and the layered material is a problem.

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14. ABSTRACT

As part of a propellant/epoxy compatibility study, double-base perforated stick gun propellant was downloaded from tank rounds subjected to temperature/humidity cycling for one month. The propellant was analyzed by traditional HPLC methods and found to have experienced no significant depletion of stabilizer. Analysis by a new desorption-GC-MS method yielded depth-profiles of nitric oxide (NO) that indicated localized decomposition at propellant surfaces. Surfaces of the propellant that had been in direct contact with a layered material (glass-reinforced RTV rubber/RTV rubber/epoxy/composite sabot) showed NO levels well in excess of baseline measurements, and a level somewhat higher than that of exterior surfaces not in direct contact with the layered material. Nitric oxide "enhancement" was observed as deep as 1-mm in from the exterior surfaces. Analysis of samples aged in the lab revealed that some of the NO generated by decomposing propellant diffuses into the silicone in the RTV rubber, thereby removing it from the autocatalytic degradation cycle and resulting in a decreased level of decomposition (as evidenced by NO levels at the core of the propellant). It was observed that uptake of NO by the silicone components was completely reversible. While the NO level at the core of the propellant was found to be lower for the samples exposed to the suspected incompatible material than for the control, elevated NO levels were found at depths up to 0.75 mm from the surface exposed to the suspected incompatible epoxy, confirming the existence of an incompatibility between the propellant and epoxy in the layered material.

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